J. Phys. Chem. A **2003,** *107,* 3295−3299

Orbital Control of the Color and Excited State Properties of Formylated and Fluorinated Derivatives of Azulene[†]

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Received: July 31, 2002; In Final Form: February 11, 2003

New azulene derivatives containing resonantly electron withdrawing formyl and resonantly electron donating fluorine substituents on the seven- as well as the five-member ring have been prepared. Systematic color changes as a result of perturbation of HOMO, LUMO, and LUMO + 1 energies were discussed. Corresponding excited-state properties related to S_2-fluorescence were determined.

Introduction

Azulene is a well-known nonalternant hydrocarbon. Its characteristic color (azure)[1] and its "anomalous" emission from the second excited state (S_2), in apparent violation of Kasha's Rule,[2] is a consequence of its unusually low-lying first excited state (S_1). The stability of S_1 is attributed to the small repulsive interaction between the two unpaired electrons that occupy different regions of the azulene chromophore rather than any intrinsic properties associated with the low-lying LUMO (lowest unoccupied molecular orbital).[3]

In a previous study of a series of methylated azulene derivatives, Heilbronner concluded that both HOMO and LUMO + 1 energy levels changed in the same direction, whereas the LUMO energy changed in the opposite direction.[4] Recently, we succeeded in tuning the color of the azulenic chromophore by introducing electronic perturbing substituents at the 1 and/or 3 positions of the electron rich five-member ring of azulene.[5] The changes in the electronic properties of these azulene derivatives were accompanied by significant changes in the their emission behavior from S_2.[6]

We now wish to report some recent findings using azulene derivatives substituted with both electron donating and withdrawing substituents on the seven-member ring as well as the five-member ring of azulene. Furthermore, parallel to the color changes, possible related changes of the excited-state properties, in particular those originated from the S_2 state, have been examined.

Experimental Section

Spectroscopy. UV−vis−NIR spectra were recorded on a Perkin-Elmer Lambda 19 or a Shimadzu UV 2401 PC spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. Steady-state fluorescence spectra were recorded on an ISS−PC1 (Champaign, IL) photon-counting spectrofluorimeter. Whenever possible absorption properties were determined in hexanes because the S_1-states are well resolved in this solvent and the 0−0 band is clearly discernable. In polar solvents, where solubilities are higher, the fine structures of the S_1-bands are usually lost. However, we chose ethanol the solvent for fluorescence measurements because of the previously reported higher quantum yield of fluorescence of **3** than in hexanes.

Fluorescence quantum yields were first determined for a HPLC-purified sample of azulene relative to anthracene (literature values for the quantum yield of anthracene in ethanol range from 0.27 to 0.306;[7] for the present work, we use the average value of $\Phi_f = 0.292$). Azulene derivatives (**2**, **3**, **9**, and **10**) were then measured relative to azulene to minimize color effects. The optical densities (OD) of all samples were measured at concentrations having an OD near 1 and then were diluted to achieve less than 0.1 absorbance to avoid errors arising from innerfilter effects.[8] All quantum yields were determined using 310 nm excitation. Emission at wavelengths greater than 320 nm was collected through a Schott (125) cut-on filter. The exciting light was polarized in the parallel (vertical) position, and the total intensity was acquired by observing the emission through parallel and perpendicular polarizer orientations ($I_{\parallel} + 2I_{\perp}$). This method avoids polarization bias due to (1) preferential response of the monochromator/detector system to one plane of polarization and (2) the intrinsic bias introduced by a right angle observation geometry.[9] Correction for the index of refraction was not necessary because all samples were measured in ethanol. Standard errors in the quantum yield determinations are estimated to be on the order of 5%. Samples were purged with dry N_2, and all experiments were at 20 °C.

Fluorescence lifetimes were determined using an ISS-K2 (Champaign, IL) multifrequency phase and modulation fluorimeter: phase and modulation data were collected at a series of light modulation frequencies as previously described,[10,11] and the data analysis was carried out using standard methods.[8] Samples were purged with dry N_2 and excited using the 351 nm line of an argon ion laser (Spectra-Physics 2045). Emission was collected through a polarizer oriented at 54.7° to the vertical laboratory access (magic angle excitation)[12] and a Schott KV372 cut-on filter which passed wavelengths greater than 360 nm. Dimethyl-POPOP (1,4-bis(4-methyl-5-phenyloxazol-2-yl)benzene) in ethanol ($\tau = 1.41$ ns) was used as a lifetime standard.

[†] Part of the special issue "George S. Hammond & Michael Kasha Festschrift".

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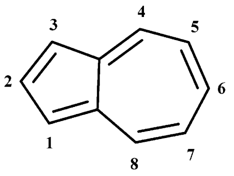
10.1021/jp021605f CCC: $25.00

All lifetimes fit well to a single-exponential decay model and standard errors were less than 5%.

Preparation of Azulene Derivatives. The procedure for the fluorination of azulene at the 1 and 3 positions was essentially the same as that described earlier using the commercially available reagent Selectfluor.[13] Mixtures of fluorinated products were separated by normal phase HPLC. 1-Formylazulene (**4**) and 1,3-diformylazulene (**5**) were prepared following published procedures.[14] 5-Formylazulene (**7**) and 6-formylazulene (**8**) were synthesized according to the procedure of Hafner starting from *N*-butyl-3-(1,3-dioxolan-2-yl)pyridinium and *N*-butyl-4-(1,3-dioxolan-2-yl)pyridinium bromides, respectively.[15] UV−vis−NIR spectra were obtained in CH_2Cl_2 for **6**−**8** and in ethanol for **9** and **10**, ^{1}H NMR spectral data for **6**−**10** were recorded in CD_2Cl_2 with tetramethylsilane as internal standard.



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2: 1-F **5**: 1,3-diCHO **8**: 6-CHO

3: 1,3-F$_2$ **6**: 1-CHO, 3-F **9**: 1-F, 6-CHO

4: 1-CHO **7**: 5-CHO **10**: 1,3-F$_2$, 6-CHO

*3-Fluoro-1-formylazulene, (**6**).* Dark blue crystals; UV−vis 310 (log ϵ 4.60), 385 (4.04), 568 (1.79) nm; ^{1}H NMR δ 10.32 (CHO, d, 1.2 Hz, 1H), 9.47 (C4−H, dd, 2.4 and 9.6 Hz, 1H), 8.51 (C8−H, d, 9.6 Hz, 1H), 7.91 (C6−H, t, 9.9 Hz, 1H), 7.87 (C2−H, s, 1H), 7.58 (C5−H, t, 9.9 Hz, 1H), 7.51 (C7−H, t, 9.9 Hz, 1H) ppm.

*5-Formylazulene, (**7**).* Dark blue crystals; UV−vis 284 (log ϵ 4.54), 297 (4.67), 322 (3.84), 388 (3.98), 564 (2.68) nm; ^{1}H NMR δ 10.06 (CHO, s, 1H), 8.87 (C4−H, s, 1H), 8.48 (C6−H, d, 9.9 Hz, 1H), 8.14 (C8−H, d, 9.9 Hz, 1H), 8.00 (C2−H, t, 3.6 Hz, 1H), 7.79 (C3−H, d, 3.6 Hz, 1H), 7.64 (C1−H, d, 3.6 Hz, 1H), 7.35 (C7−H, t, 9.9 Hz, 1H) ppm.

*6-Formylazulene, (**8**).* Blue-green crystals; UV−vis 289 (log ϵ 4.81), 336 (3.56), 352 (3.72), 368 (3.66), 654 (2.48) nm; ^{1}H NMR δ 10.11 (CHO, s, 1H), 8.56 (C4−H and C8−H, d, 9.9 Hz, 2H), 8.12 (C2−H, t, 3.6 Hz, 1H), 7.73 (C5−H and C7−H, d, 9.9 Hz, 2H), 7.53 (C1−H and C3−H, d, 3.6 Hz, 2H) ppm.

*1-Fluoro-6-formylazulene, (**9**).* Green crystals; UV−vis 287 (log ϵ 4.78), 337 (3.46), 354, (3.57), 368 (3.25), 706 (2.36) nm; ^{1}H NMR δ 10.04 (CHO, s, 1H), 8.43 (C8−H, d, 9.6 Hz, 1H), 8.39 (C4−H, dd, 3.4 and 9.6 Hz, 1H), 7.72 (C2−H, d, 4.5 Hz, 1H), 7.56 (C5−H and C7−H, t, 9.6 Hz, 2H), 7.30 (C3−H, t, 4.5 Hz, 1H) ppm.

*1,3-Difluoro-6-formylazulene, (**10**).* Pale green crystals; UV−vis 275 (log ϵ 4.67), 336 (3.67), 344 (3.63), 352 (3.62), 367 (shoulder, 3.36), 738 (2.41) nm; ^{1}H NMR δ 9.89 (CHO, s, 1H), 8.27 (C4−H and C8−H, d, 9.6 Hz, 2H), 7.28 (C5−H and C7−H, d, 9.6 Hz, 2H), 7.27 (C2−H, s, 1H) ppm.

Results and Discussion

Electron Distribution in the Low-Lying MO's of Azulene. The probabilities of locating a single electron in the HOMO and the two low-lying LUMOs of the nonalternant hydrocarbon azulene (square of the coefficients) are shown graphically in Figure 1 (AM-1, Hückel MOs).[5] For comparison, the probabilities of locating electrons in the HOMO and LUMO of the isomeric alternant hydrocarbon, naphthalene, are also shown in the figure.[1a] The HOMO and LUMO + 1 of azulene have very similar electron distributions. In contrast, the electron distribution in the LUMO of azulene is substantially altered. In this MO, the 1 and 3 positions are essentially void of electron density with substantial charge transfer to the seven-member ring. For the alternant hydrocarbon naphthalene, the electron distributions are unchanged in going from HOMO to LUMO. The different location of electrons in the HOMO and LUMO orbitals of azulene means a small repulsive interaction between the electrons in these orbitals, i.e., in the S$_1$ state of azulene (although they are confined within a similar C10 molecular framework as naphthalene). In contrast, there is a much larger repulsive energy between the same electrons in naphthalene. The much smaller S$_0$−S$_1$ energy gap for azulene compared to that of naphthalene accounts for the well-known color difference between azulene (blue) and naphthalene (colorless).

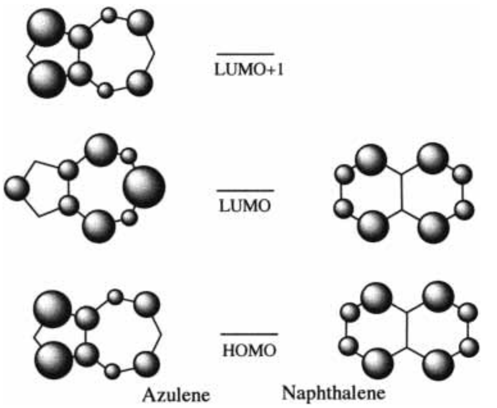

Figure 1. Probability of locating an electron (square of coefficients of the wave functions) in the HOMO, LUMO, and LUMO + 1 of azulene (left) and naphthalene (right).

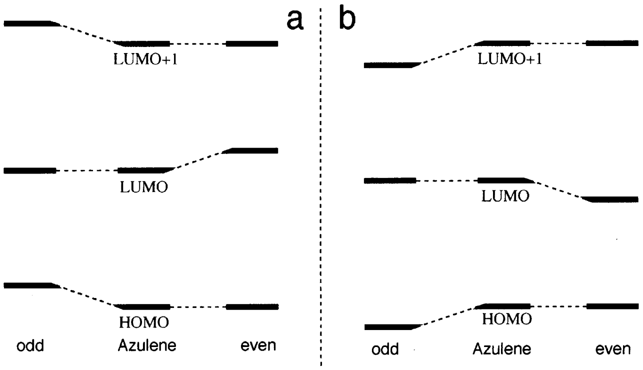

Figure 2. Effect of substituents on the energy levels of HOMO, LUMO, and LUMO + 1 of azulene, a qualitative description reflecting effect of substituents on the MO levels. (a) Electron donating substituents when located on an odd numbered (**1**, **3**, **5**, or **7**) or even numbered (**2**, **4**, **6**, or **8**) carbon atoms of azulene. (b) Electron withdrawing substituents when located on an odd or even numbered carbon atoms of azulene.

Methyl-Substituted Derivatives of Azulene. The large difference in electron distributions in the HOMO and LUMO of azulene suggests the possibility of attenuating the energy levels of these MOs and the corresponding excited state by strategically attaching electron-donating or withdrawing substituents to different ring positions. Thus, electron donating substituents at the 1, 3, 5, or 7 positions should raise the energy level (high electron density at these centers) without affecting the LUMO energy significantly (zero or low electron density at these positions). This alteration should lead to a decrease of the S$_0$−S$_1$ energy gap and an increase of the S$_1$−S$_2$ gap (Figure 2a). In contrast, electron-withdrawing substituents should have the opposite effect (Figure 2b). This possibility was demonstrated by Heilbronner and co-workers in their study of the absorption properties of a series of methylated azulene deriva-

TABLE 1: Spectral Shifts (λ_{Max}) in Azulenes with Inductively Donating (Methyl), Resonance Donating (Fluoro), and Withdrawing (−CHO) Substituents[a]

	S_1-S_0 transition	
compound	ν_{max} (cm^{-1})	$\Delta\nu_{max}$
azulene[b]	17 241	
1-methyl[b]	16 450	−791
2-methyl[b]	17 670	+429
4-methyl[b]	17 610	+369
5-methyl[b]	16 890	−351
6-methyl[b]	17 700	+459
1-fluoro[c]	16 000	−1241
1,3-difluoro[c]	14 920	−2321
1-CHO	18 450	+1209
1,3-Di-CHO	19 724	+2483

[a] In hexane.[5] [b] From ref 4. [c] From ref 6.

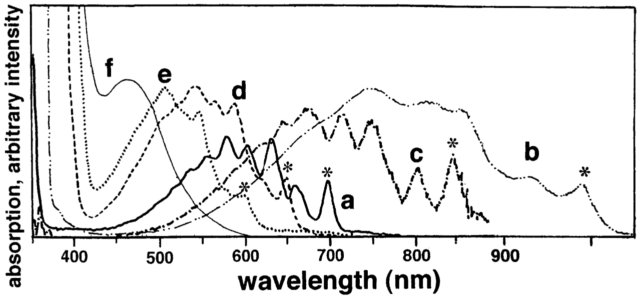

Figure 3. S_1 band and the "blue-window" of azulene, **1**, (line a) and substituted azulenes (line b, 1,3-difluoro-6-formyl, **10**; line c, 1,3-difluoro, **3**, line d, 1-formyl, **4**; line e, 1,3-diformyl, **5**; line f, **5** in trifluoroacetic acid), all recorded in hexanes. The asterisk indicates positions of the 0−0 band.

tives[4] as shown by the data in Table 1. Methyl groups on the 1 or 5 positions clearly have the opposite effect on the S_0-S_1 transition energy compared to methyl substitution on the 2, 4, or 6 positions.

Color Changes in Substituted Azulenes. Changes in electronic excitation energy could lead to dramatic changes in the perceived color of a compound. However, for that to occur, a larger perturbation on the MOs must occur, more than that provided by the weakly electronic-donating (inductive) methyl groups. In a preliminary study, we demonstrated the possibility of tuning the color of the azulene chromophore by attaching strong resonance donating or withdrawing substituent(s) at the 1 and 3 positions of the five-member ring of azulene.[5] Thus, for 1,3-difluoroazulene, the S_0-S_1 was found to be significantly red-shifted ($\Delta\nu_{max} = -2321$ cm^{-1}) with very little change in the S_2 band position. The result was an unusually large separation of the upper S_1-S_2 gap (15 870 cm^{-1}). The widening of this gap which gives azulene its characteristic blue color permits transmission of more yellow light (Figure 3), thus giving a green tinge to 1,3-difluoroazulene. As expected, 1-fluoroazulene has an intermediate value for its S_1-S_2 transition energy (Table 1), and its color is blue. On the other hand, attachment of electron-withdrawing aldehyde groups to the 1 and 3 positions of azulene results in a substantial narrowing of the S_1-S_2 band gap and closing of the blue window of transparency for unsubstituted azulene. In this case, the compound appears red because only light of $\lambda > 610$ nm is transmitted (Figure 3). Not too surprisingly, the S_1-S_2 window of 1-formylazulene (**4**) remains partially open to allow the transmission of both blue and red light giving it a maroon color.

We have now broadened this method of selective perturbation of MOs as a means of tuning the color of the azulenic chromophore by introducing additional substituents on both the seven- and five-member rings of azulene.

For this series of compounds, the first pure green azulene crystals are seen in the form of 1,3-difluoroazulene (**3**), 1-fluoro-6-formylazulene (**9**), and 1,3-difluoro-6-formylazulene (**10**) (pale green). An electron-withdrawing substituent on the 6 position is predicted to stabilize LUMO while not affecting the energies of the HOMO or LUMO + 1. Thus, the pale green color of 1,3-difluoro-6-formylazulene (**10**) can be rationalized on the basis of a large spectral red-shift of the S_1 band (0,0 peak at 10 200 cm^{-1} or a $\Delta\nu_{max} = -3870$ cm^{-1} from azulene) brought about by the combined energy-perturbing effects of the resonantly electron-donating fluorine substituents at the 1 and 3 positions and the electron-withdrawing CHO substituent at the 6 position. The S_1 band is now mostly in the NIR region (Figure 3). We reasoned that an electron-withdrawing substituent on an odd-numbered carbon of the seven-member ring should blue-shift the S_1 band for the same reasons as for the 1- or 3-CHO examples above. Thus, the blue-shifted S_1 band at 15 290 cm^{-1} of 5-formylazulene (**7**) and the red-shifted S_1 bands of 2-,[16] 4-,[17] and 6-formylazulene (**8**) (relative to azulene) are consistent with our model of orbital control of spectral properties of azulene derivatives.

As a further test of the orbital control model, we compared the reported S_1 band position in 1,3-difluoroazulene (**3**) and 1,3-difluoro-6-isopropylazulene.[6] Gratifyingly, the presence of an electron-donating alkyl substituent on the 6 position results in a spectral blue shift for the S_1 band consistent with destabilization of LUMO relative to HOMO.

Last, 3-fluoro-1-formylazulene (**6**) is blue compared to the maroon color of the nonfluorinated 1-formylazulene (**4**). The stabilizing effect of the fluorine substituent on the HOMO and LUMO + 1 energies apparently countermands the influence of the aldehyde groups at the 1 position. Interestingly, 1-fluoro-6-formylazulene (**9**) is green, whereas the isomer 3-fluoro-1-formylazulene (**6**) is blue, demonstrating opposite orbital control by relocating the formyl substituent from the seven- to the five-member ring. At C-6, the CHO group destabilizes HOMO, causing a more red-shifted S_1 band.

We also studied changes in the spectral properties and color of both 1-formylazulene (**4**) and 1,3-diformylazulene (**5**) in a moderately strong organic acid, trifluoroacetic acid (pK_a 0.3). Under these conditions, protonation of the aldehyde was expected to enhance its electron-withdrawing ability and induce a blue shift in the S_1 band by stabilizing its HOMO. Very little spectral change was observed for the monoaldehyde (**4**) indicating that the single aldehyde group was not appreciably protonated in trifluoroacetic acid. However, for dialdehyde (**5**), addition of a small amount of trifluoroacetic acid produced an immediate color change of red to yellow. In its UV spectrum the S_1 band ($\Delta\nu_{max} = -4400$ cm^{-1}) was strongly blue-shifted and appeared almost as a shoulder on the S_2 band (Figure 3). Upon neutralization with triethylamine, the color reverted back to its original red color indicating that the protonation was reversible. Apparently, the presence of both aldehyde groups is necessary for monoprotonation to occur and the second protonation step to the diprotonated species is far less likely.

In our hands, the use of stronger acids such as sulfuric acid or perchloric acid led to irreversible changes in the UV spectra indicating degradation of the starting material.

Excited-State Properties of Azulenes: S_2 Emission. Azulene is well-known for its "anomalous" dominant S_2 fluorescence. The large S_1-S_2 energy gap of azulene, nearly identical to that of S_1-S_0, is believed to be the primary factor that

TABLE 2: Absorption Maxima and Extinction Coefficients of Substituted Azulenes

compound	solvent	color	λ_{max} (S$_2$), nm	ϵ (S$_2$), 10^3(M^{-1}cm^{-1})	λ_{max}(S$_1$), nm	ϵ(S$_1$), 10^2(M^{-1}cm^{-1})	S$_1$(0−0), 10^3cm^{-1}
azulene **1**	hexanes	blue	341	4.01	580	3.48	14.33
	EtOH		340	4.20	576	3.62	14.47
1-CHO **4**	hexanes	maroon	385	1.00	542	4.67	15.43
1-F **2**	hexanes[a]	blue	343	3.26	625	3.23	13.02
	EtOH		341	3.54	618	3.52	13.16
1-CHO, 3-F **6**	hexanes[b]	blue	398	8.91	590	5.37	14.02
	CH_2Cl_2		386	10.81	568	6.25	14.28
2-CHO **11**	hexanes[c]	green	360	6.31	664	1.55	
4-CHO **12**	hexanes[d]	green	354	1.95	642	3.55	
5-CHO **7**	hexanes	violet	383	9.01	571	4.50	14.51
6-CHO **8**	hexanes	blue-green[e]	351	5.75	652	3.63	12.34
1-F, 6-CHO **9**	EtOH	green[e]	354	3.71	706	2.29	11.23
1,3-F$_2$ **3**	hexanes[a]	green[e]	342	3.29	670	1.44	11.88
	EtOH		341	3.39	665	2.51	12.72
1,3-F$_2$,6-CHO **10**	hexanes	pale green[e]			750		10.13
	EtOH		336	4.67	738	2.57	10.39
1,3-(CHO)$_2$ **5**	hexanes	red			507		16.64
	CH_2Cl_2		384	10.55	486	8.20	17.54
	CF_3COOH	yellow	374	12.05			

[a] From ref 6. [b] From ref 19. [c] Reference 16. [d] Reference 17. [e] Blue in solution.

TABLE 3: Quantum Yield of Fluorescence (Φ_f), Lifetime (τ), Rates of Fluorescence (k_r), and Nonradiative Decay (k_{nr}) from the S$_2$ State of Several Substituted Azulenes[a]

compound	Φ_f	τ/ ns	k_r/ 10^7 s^{-1}	Σk_{nr}/ 10^8 s^{-1}	log(Σk_{nr})	ΔE(S$_2$−S$_1$) 10^3cm^{-1}
Az **1**	0.035	1.3	2.7	7.4	8.87	14.02
1-F **2**	0.04	1.8	2.2	5.4	8.73	15.01
1-F, 6-CHO **9**	0.01	1.9	0.5	5.2	8.72	15.36
1,3-F$_2$ **3**	0.16	10.3	1.6	0.8	7.91	15.87
1,3-F$_2$, 6-CHO **10**	0.01	7.1	0.14	1.3	8.11	16.85

[a] In ethanol.

contributes to the unusually long lifetime of the upper state. Interestingly, the S$_1$ state with an equally large gap from S$_0$ is extremely short-lived. A recent theoretical study suggests that its short lifetime is due to the presence of a chemical channel of deactivation (ring puckering), a conical intersection facilitating its rapid decay.[18] For 1,3-difluoroazulene (**3**), the reduced S$_1$−S$_0$ state (by > 2000 cm^{-1}) led to a further increase of energy separation between S$_1$ and S$_2$ states (15 870 cm^{-1}), creating an unprecedented reversal of energy gaps between the three lowest singlet states [$\Delta\Delta E$ (S$_2$−S$_1$)−(S$_1$−S$_0$)] by ~4000 cm^{-1}. Therefore, it was not surprising to find an exceptionally large fluorescence yield (up to 20%) and a long fluorescence lifetime (10 ns) originating from its S$_2$ state.[6]

To test the possible presence of a correlation between the color of a substituted azulene (related to the energy gap between S$_2$ and S$_1$ states) with its S$_2$-fluorescence characteristics, we have now determined the fluorescence quantum yields and lifetimes, and calculated the rates of radiative (k_r) and radiationless decay (k_{nr}) from the S$_2$ states of most of the above-mentioned color compounds. The results are summarized in Table 3.

Formylazulenes generally have greatly reduced quantum yields of fluorescence relative to azulene itself. For example, Φ_f for fluorinated 6-formylazulenes (**9**, **10**) were only about one tenth of the corresponding fluoroazulenes (**2**, **3**). For 1-formylazulene (**4**), 3-fluoro-1-formylazulene (**6**), and 1,3-diformylazulene (**5**), although the fluorescence spectra could be recorded, its quantum yields were too small to be measured with any certainty (est. to be ≤0.002). The weak fluorescence is however not due to the reduced average lifetime. The radiative rate constants for 1-fluoro-6-formylazulene (**9**) and 1,3-difluoro-6-formylazulene (**10**) have been calculated using the standard expressions: $k_r = \Phi_f/\tau$ and $\Sigma k_{nr} = (1 - \Phi_f)/\tau$. The k_r values have decreased significantly (Table 3) from the corresponding azulenes and fluoroazulenes. We suspect that the most likely cause for the change of radiative decay is the involvement of the n,π* state in these compounds, which is likely to lie closely to the S$_2$ state. (Determination of its exact position was unfortunately difficult because of the expected low intensity, further obscured by the strong S$_2$ band.) Hence, collectively, these aldehydes present an interesting case. Their color changes are sensitive to the electron-withdrawing character of the aldehyde group and not to the presence of an extra, close lying electronic state (too low a transition probability to have an effect) but rather due to π-orbital control associated with this substituent. At the same time, the widened blue-window, in the case of **10**, does not guarantee a long-lived S$_2$ state. In fact, the opposite is true. The shortened S$_2$ lifetime is likely due to new decay channel(s) provided by the nearby n,π* state. Unfortunately, instrument limitation does not allow simultaneous determination of triplet yields of these compounds.

Acknowledgment. The work was supported by a grant from U.S. Army Research Offices (DAAH19-99-1-0205).

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